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COMPATIBILITY OF TITANIUM AND TITANIUM ALLOYS WITH LIQUID AND GASEOUS OXYGEN IN MISSILE PROPELLANT SYSTEMS

MRG 232

June 7, 1961

Prepared by: J.E. Chafey

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REPORT MRG 232

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SUBJECT: "Compatibility of Titanium and Titanium Alloys With Liquid and Gaseous Oxygen in Missile Propellant Systems"

ABSTRACT: A review has been made of the published information regarding the reaction of titanium and titanium alloys with liquid and gaseous oxygen. Results of tests conducted at Astronautics at an earlier date are in agreement with those of other investigators. Titanium must be classed as "impact sensitive" to liquid oxygen according to the ABMA-type compressive impact test. However, on the basis of somewhat more practical tests conducted both at Astronautics and elsewhere, which simulate more closely the conditions of service in a missile propellant system, it must be concluded that titanium and its alloys may be used safely in such systems. This includes conditions of pressure and pressure surges, rapid flow, use of quick-acting valves, occurrence of accidental damage, rupture, etc. Ignition of the titanium-oxygen reaction is not spontaneous. It requires that several unique conditions must be met at approximately the same instant. These conditions do occur in the compressive impact test for both titanium and aluminum (the latter is used regularly for liquid oxygen service) but should not occur in the liquid oxygen system of liquid-fueled missiles.

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SUBJECT: Compatibility of Titanium and Titanium Alloys With Liquid and Gaseous Oxygen in Missile Propellant Systems.

INTRODUCTION:

Considerable attention has been focused upon the reactivity of titanium with oxygen during the past two years. As a result of two instances of apparent sensitivity which occurred in 1959 (at North American-Rocketdyne and at Aerojet-General) investigations have been carried out by a number of companies and research institutions in order to determine the conditions necessary for the reaction to occur, and thereby, to more clearly define the extent of compatibility.

Most of the data generated to date have resulted from compressive impact tests. Such tests were conducted at General Dynamics/Astronautics and at Aerojet-General, Battelle, ABMA, Martin-Denver, WADD Propulsion Laboratory, North American Rocketdyne, and Reaction Motors. General Dynamics/Astronautics also conducted two additional types of tests: (a) diaphram puncture tests in LO_2, and (b) surge tests using gaseous O_2 at 65 psig. Other pertinent tests, as described briefly below, were done by several of the companies mentioned.

In view of the widespread interest in the reaction sensitivity of titanium in gaseous and liquid oxygen the Defense Metals Information Center at Battelle has collected the available facts and published several reports (see list of references) which summarize the work to date.

DISCUSSION:

The North American and Aerojet-General incidents referred to above could not be fully explained. In both cases Ti-LO_2 reactions were reported to have occurred when the tests were unattended. Hence, the conditions which initiated the reaction are not known.

Although it is felt that not all of the facts have been fully established regarding this important subject, and that further investigative work is warranted, nevertheless there appears to be substantial agreement on the following conclusions:

1. Under certain conditions of compressive impact titanium and its alloys can be made to react violently with liquid or gaseous oxygen. The reaction is highly exothermic and in some instances it may proceed until either the titanium or the oxygen is entirely consumed.

2. In spite of this "impact sensitivity" titanium may be used with a high degree of safety in liquid oxygen systems when due care and precaution

are exercised. For example, foreign particles, grease, etc. which can themselves react with LO_2, and thereby might initiate reaction of titanium with LO_2, must be scrupulously excluded. It may be pointed out that the same cleanliness precautions are required where other metals are concerned in LO_2 systems, since under some conditions all metals may be made to burn in LO_2. Aluminum, which is used in many liquid oxygen systems (Titan Missile tanks, Atlas anti-slosh baffles) displays liquid oxygen "impact sensitivity" when tested in compressive impact in a manner similar to that of titanium.

3. The titanium-liquid oxygen reaction is not spontaneous, and several conditions must be met at approximately the same instant in order to initiate and propagate the reaction. Normal conditions of contact of titanium and liquid oxygen, whether static or dynamic, are not sufficient to initiate the reaction.

4. Test conditions other than compressive impact have not resulted in reaction. The diaphram puncture tests conducted at General Dynamics/Astronautics and elsewhere (see references 1, 2, 3 and 6) demonstrated that titanium, aluminum and similar "impact sensitive" materials could be ruptured while in contact with liquid oxygen without occurrence of reaction. Similar rupture tests were conducted at Battelle with the same result. Tensile rupture tests in liquid oxygen at slow fracture rates and at rapid rates were also conducted at Battelle, Titanium Metals Corporation, Aerojet-General, and Martin. In each case it was demonstrated that formation of a fresh, unoxidized surface in the presence of liquid oxygen is not sufficient to promote reaction. In some instances a flash of light was reported, but there was no evidence of burning on the fracture surfaces. Similar tensile fracture tests were conducted in gaseous oxygen at Battelle and at Stanford Research Institute. Reaction occurred upon fracturing the sample only when the oxygen was present under a pressure of approximately 300 psi or greater.

5. Experiments with high LO_2 pressures at Battelle, such as those generated by a water-hammer type of impact, did not initiate reaction. Similar results were obtained when a ½" diameter titanium tube filled with LO_2 was smashed by a 66 ft-lb impact. It was also shown that LO_2 could be forced through a small hole in a titanium sheet specimen at a velocity estimated to be several thousand ft/sec without occurrence of the titanium-oxygen reaction. The gaseous oxygen surge tests at General Dynamics/Astronautics also demonstrated that materials that were judged "impact sensitive" by the LO_2 compressive impact test could, nevertheless, be subjected to a gaseous oxygen pressure surge of 0 to 65 psig without reaction.

6. Most of the work described in the references was done with either unalloyed titanium or with Ti-5Al-2.5Sn alloy. It may reasonably be assumed that all of the titanium alloys will behave in a similar manner.

7. Results of the various experiments reviewed by the Defense Metals Information Center has provided a basis for a plausible explanation of the mechanism of the Ti-LO_2 reaction, as follows:

a. Initiation of the reaction requires an input of high, local energy such that the temperature of the reactants can reach some high threshold value at the local area;

b. the reaction proceeds only when the oxygen is in the gaseous condition; but, of course, this may be readily generated, as by the highly localized heat of compressive impact;

c. the gaseous oxygen, present or generated on the surface by the heat of impact, must be compressed and brought into intimate contact with the titanium surface;

d. the force which generates the heat, i.e. compressive impact, must also expose a fresh, unoxidized surface on the titanium which can then react with the compressed gaseous oxygen.

Thus according to this explanation, several conditions must be met at approximately the same instant to initiate and propagate the titanium-liquid oxygen reaction. These conditions are met in the ABMA-type compressive impact test, but are not met in the several other somewhat more practical tests conducted. It may be noted, too, that presence of grit, foreign material, rough surfaces, etc. would increase "impact sensitivity" by creating the condition for high local friction to initiate the reaction, as explained above.

SUMMARY:

By way of summary, then, the following points may be cited.

1. Titanium and its alloys (and also aluminum alloys) may be classed as liquid oxygen impact sensitive according to the ABMA-type compressive impact test.

2. Titanium may be used safely in liquid oxygen systems under the usual conditions of cleanliness, which excludes the presence of combustible materials.

3. Titanium may be fractured in the presence of LO_2 without reaction.

4. Titanium is suitable for normal conditions of contact with liquid or gaseous oxygen in missile systems. This includes conditions of pressure and pressure surges, rapid flow, use of quick acting valves, etc.

5. Accidental damage due to external impact against titanium LO_2 tanks, ducts, tubes, etc., should present no greater hazard than in the case of similar accidents to aluminum or stainless steel systems.

6. Initiation of the Ti-LO_2 reaction is not spontaneous but, rather, requires that several unique conditions must be met at approximately the same instant. These conditions do occur in the compressive impact test (ABMA-type), but should not occur in the liquid oxygen missile system.

REFERENCES:

1. Boyd, W. K., "Summary of Present Information on Impact Sensitivity of Titanium When Exposed to Various Oxidizers", Defense Metals Information Center, DMIC Memorandum 89, March 6, 1961.

2. Jackson, J. D., and Miller, P. D., Boyd, W. K., and Fink, F. W., "A Study of the Titanium-Liquid Oxygen Pyrophoric Reaction", WADD TR60-258, Project 7351, Battelle Memorial Institute, Contract AF33(616)-6345, March 1960.

3. "Preliminary Data on the Reaction Sensitivity of Titanium and Oxygen", Defense Metals Information Center, August 14, 1959.

4. Hertz, J., "Oxygen Impact Sensitivity as a Criterion for Material Selection", Convair Report Number MRG-214, February 2, 1961.

5. Hertz, J., "Modified LO_2 Impact Tests", Convair Report Number MRG-207, January 10, 1961.

6. Boyd, W. K., and White, E. L., "Compatibility of Rocket Propellants with Materials of Construction", Defense Metals Information Center, DMIC Memorandum 65, September 15, 1960.

7. Littman, F. E., and Church, F. M., "A Study of Spontaneous Ignition of Metals", Stanford Research Institute, Menlo Park, California, Final Report, April 1, 1959 to July 31, 1960, SRIA-29, SRI Project Number SU-2887.

8. Beane, G. A., "Results of Impact Testing of Titanium With Liquid Oxygen", Propulsion Laboratory, Wright Air Development Center, ARDC, Wright-Patterson Air Force Base, Ohio, WADC TN 59-175, April 1959.

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